



Soil Bentonite Liner to Control Migration of Iron and Lead Ions

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ABSTRACT

Compacted soil liners amended with bentonite are widely used to minimize migration of ions like iron and lead. The thickness of the liner for a minimum period is arrived based on the rate of migration of contaminants through the liner. The rates of contaminant transport depends both on the hydraulic consideration as well as diffusion rates, which vary with the type of contaminant and the compacted soil liner. The advection diffusion mathematical equation is used to assess the transport of contaminants through soil knowing the soil condition and hydraulic head. It requires the knowledge of transport parameters viz., diffusion coefficient and retardation factor of contaminating ions in the liner. These transport parameters can be obtained by breakthrough curves using soil column test. In this study, it is proposed to obtain breakthrough curve of iron and lead ions in locally

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available soil amended with 10% bentonite. Mathematical models with assumed values of transport parameters are used to generate theoretical breakthrough curves. The set of values which yield the theoretical curves close to experimentally determined breakthrough curves are obtained for the given iron and lead ions through the bentonite amended soil liner. The values are used to determine the break through times for any thickness of the liner.

Keywords: Breakthrough curve, Break through time, Column test, Diffusion Coefficient, Retardation Factor

1. INTRODUCTION

Heavy metals are released frequently from different sources, for example, material, stockpiling batteries, electro plating commercial ventures and so on. Heavy metals despite the fact that at low fixation are considered as lethal and in this way bringing about ecological issues and are risky to human wellbeing and environment. Strong waste landfills constitute a potential real danger to the ground water due to these substantial metals.

Heavy metals, for example, iron and lead are ordinarily found in waste and consequently display in landfill leachates and ground water. In Indian urban areas, open, uncontrolled and ineffectively oversaw dumping is generally worked on, offering ascent to genuine natural issues. Strong waste in urban communities and towns are straightforwardly arranged off ashore in an unacceptable way and thus there is a risk to ground water quality and brought about ground water defilement. Likewise the iron and lead are drained from the waste dumped in landfills and centralizations of iron and lead are normally found in leachates. Consequently in numerous real urban communities heavy metals are quickly getting into the groundwater. Metals added to soil will regularly be held at the dirt surface.

Migration of iron and lead ions from waste dump site or unengineered landfills is a common source for iron and lead ions in the ground water. Soil liners are generally used to minimize migrations of contaminants including metal ions. Soils generally have large sorption capacity and reduce the migration of contaminants. These liners are preferred because of their low cost, large leachate attenuation capacity and resistance to damage and puncture.

A relatively small amount of bentonite can lower the hydraulic conductivity to considerable extent. Addition of 4-5% sodium bentonite soil drops the hydraulic conductivity from 10^{-4} to 10^{-7} cm/sec. Calcium bentonite also can be used as an additive in soil liner.

Adsorption of soluble metallic species by clays, oxides and other colloidal matter appears to be an important means of controlling the trace soluble metal concentration in the system. Liners for landfills should be such that they are capable of minimization of leachates containing metal ions such as iron and lead. The retention mechanisms for metals added to soil include adsorption of the metal by the soil solid surfaces and precipitation. The retention of cationic metals by soil has been correlated with such soil properties such as surface area, cation exchange capacity, organic matter content, clay content, iron and manganese oxide content, and carbonate content. Anion retention has been correlated with iron and manganese oxide content. It is reported that in addition to soil properties, the other parameters like type of metal, its concentration, the presence of competing ions play an important role in the retention of heavy metal ions. (Maya Naik and Sivapullaiah, 2003, Sivapullaiah)

Soil Liner to retard the movement of heavy metal in the leachate

The requirements of clay liners are

- 1) Liners should possess high sorption capacity
- 2) The clay barrier shall be compatible with the leachate to be contained.
- 3) From a chemical flux point of view, 10^{-8} cm/s is preferable since diffusion often becomes the dominant migration mechanism.
- 4) Can plug the pore space in natural soil such that large channels for contaminate transport are effectively eliminated

Compacted Natural clay as liner

Clay is the most important component of soil liner because it ensures low hydraulic conductivity. The soil should have 20% silt and clay, plasticity index should be greater than 10%. The material should not contain soil particles larger than 1 to 2 inches in diameter which may form a permeable layer. Clays possess sorptive and or attenuative capacity and reduce the capacity of contaminants in the leachate. But some soils do not provide an impermeable boundary. To achieve this, bentonite is amended to natural soils and compacted.

Knowing the effective diffusion coefficient (D_e) it is possible to calculate the rate of migration of species using the above equation. It is proposed to determine the break through times for a given thickness for iron and lead for soil amended with bentonite which are used as liners after proper compaction.

Contaminant Transport Modelling

Contaminant transport through compacted soil is controlled by a variety of physical, Chemical and Biological processes. The physical processes include diffusion, advection and dispersion. The chemical process usually includes sorption, dissolution, complexation, hydrolysis/substitution and oxidation. The biological process includes decay etc. In order to predict the transport of iron and lead pollutant specie, the transport parameters involved in the governing set of equations that describes the transport processes need to be accurately defined. The laboratory column experiments, which can be used to estimate the transport parameters of chemicals species migrating through waste contaminant barriers. (Folkes, D.J. 1982)

1.1 Contaminant transport processes through soil liner

It is impossible to practically provide complete contamination of leachate generated in a waste landfill facility. Hence the design of a suitable (either as a primary barrier for municipal waste site or as a backup barrier for hazardous waste) barrier requires an estimation of potential rate of contaminant transport through clay liner of landfill in the design of secure waste storage facility. The following physical and chemical processes usually govern the contaminant transport (Freeze, R.A. and Cherry, J.A.1979).

1.1.1 Advection - Advection (convection) is the process by which solutes are transported along with the flowing fluid or solvent. Due to advection, non-reactive solutes travel at an average rate equal to the seepage velocity of the pore fluid.

1.1.2 Diffusion- Diffusion is the transport process in which a chemical or chemical species migrate in response to a gradient in its concentration.

1.1.3 Dispersion - Dispersion refers to the spreading and mixing caused by the variation in velocity with which water moves.

1.2 Determination of diffusion coefficients by column experiment

For predicting the effective diffusion coefficients of ionic species of interest using column experiments, the below equation is used. The column experiment results are commonly reported in terms of number of pore volumes that have passed through packed soil column wherein one pore volume, is the cross sectional area of column(A) times its length(L) times the porosity(n) i.e., ALn .

Total number of pore volume U is the total discharge divided by value of one pore volume

$$U = \frac{vnAt}{ALn} = \frac{vt}{L}$$

Thus with these definitions, the one dimensional approximate Ogata-Banks equation can be rearranged as:

$$\frac{C}{C_o} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{1-U}{2\sqrt{UD_e/vL}} \right) \right]$$

$$J_{0.84} = \left[\frac{(U-1)}{U^{1/2}} \right] \quad \text{when } \frac{C}{C_o} = 0.84$$

$$J_{0.16} = \left[\frac{(U-1)}{U^{1/2}} \right] \quad \text{when } \frac{C}{C_o} = 0.16$$

$$D_e = \frac{vL}{8} [J_{0.84} - J_{0.16}]^2$$

1.3 Retardation factor

The migration of contaminants caused by the movement of chemicals dissolved in the water is described by the retardation factor. Attenuation of leachate contaminant species is one of important criteria for the choice of landfill liner (Drury, D., 1997). The retardation factors for any particular chemical include all the interactions between the many chemical species and the solid surfaces of the porous media. These interactions tend to retard the migration of the chemical behaviours need to be known.

Retardation factor, R_f , can be determined in flow experiment where R_f for particular species is the ratio of solution velocity to the contaminant velocity. The retardation factor for that species is given by

$R_f = V_{gw}/V_{sp}$ Where V_{gw} is the velocity of the water and V_{sp} is the velocity of the contaminant species

Role of retardation factor in the prediction of experimental breakthrough curves of ions in soil

The breakthrough curves are drawn using advection diffusion equations considering experimentally determined effective diffusion coefficients. It has been observed that effective diffusion coefficient alone is not sufficient to predict breakthrough curves. To enhance the predictive capability, retardation factor, R_f that accounts all the retardation processes that occur while the ions are passing through soil is considered in the Ogata-Bank's equation.

Theoretically the breakthrough curves are important to reasonably assess the retardation factor, R_f from the detailed account of transport processes. The theoretical breakthrough curves for different ions are obtained using Ogata-Bank's equation

$$\frac{C}{C_o} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{R_f x - vst}{2\sqrt{(D_e t R_f)}} \right) + \exp \left(\frac{R_f v_s x}{D_e} \right) \operatorname{erfc} \left(\frac{R_f x + vst}{2\sqrt{(D_e t R_f)}} \right) \right]$$

Calculated values of diffusion coefficients are determined by various methods, knowing velocity (v), and thickness of soil column used in the experiment and for different values of retardation factors have been developed with the MATLAB. The values of retardation factor, which gives theoretical curves close to the experimental breakthrough curve, are obtained.

1.4 Analytical solutions to One Dimensional Contaminant Transport Equations

Method used to solve the one dimensional governing equation, analytical methods are widely used for calculating the contaminant migration. The best known analytical solution for concentration C at time t and depth x beneath the surface of a barrier, which is assumed to be infinitely deep and subject to a constant surface concentration, C_o can be calculated. (Ogata 1970)

C_o is calculated by

$$\frac{C}{C_o} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{R_f x - vst}{2\sqrt{(D_e t R_f)}} \right) + \exp \left(\frac{R_f v_s x}{D_e} \right) \operatorname{erfc} \left(\frac{R_f x + vst}{2\sqrt{(D_e t R_f)}} \right) \right]$$

1.5 Determination of effective diffusion coefficients

The column method is used to calculate transport parameter and it is most preferred and is described here. This soil column test, traditionally known as leaching column test and has been used to study the adsorption and migration of contaminants through clay barriers. Firstly steady state flow is established through the soil sample by using distilled water in source reservoir. After steady state fluid has been established, the fluid in the influent reservoir is changed to a solution to a known and constant concentration (C_o) of particular chemicals constituents. The concentration (C) in the effluent reservoir is measured as the data are reduced in the form of break through curves, the breakthrough curves are modelled using analytical solutions and hence the, Diffusion coefficient can be calculated by knowing C , C_o , v , L . The following methods describe some of the more common procedures, which have been used to calculate the transport parameters.

1.5.1 Ogata Bank's Method

In this method a plot of relative concentration versus time or number of pore volume are plotted from the time ($t_{0.16}$) corresponding to $C/C_o = 0.16$ and time ($t_{0.84}$) corresponding to $C/C_o = 0.84$ are obtained using these values and knowing the thickness of soil (L) and knowing the value of velocity, effective diffusion coefficient is calculated.

$$U = vt/L$$

$$J_{0.84} = \left[\frac{(U-1)}{U^{1/2}} \right] \quad \text{when } \frac{C}{C_o} = 0.84$$

$$J_{0.16} = \left[\frac{(U-1)}{U^{1/2}} \right] \quad \text{when } \frac{C}{C_o} = 0.16$$

$$D_e = \frac{vL}{8} [J_{0.84} - J_{0.16}]^2$$

1.5.2 Time Lag Method

In this method, the total amount of diffusion substance per cross sectional area, Q_t is plotted versus time and determining the values for the intercept, T_L then diffusion coefficient, D , is calculated from the equation,

$$T_L = \frac{L^2}{6D}$$

1.5.3 Root - Time Method

In this method, the time corresponding to relative concentration of 0.1 (90% equilibrium) is obtained from the breakthrough curve of the species. Then diffusion coefficient, D , is calculated using the equations,

$$D = \frac{0.2436 L^2}{t_{90}}$$

1.6 Migration of ions in soil liner below landfill under given field condition

From the data obtained for iron and lead ions in proposed liner viz., the retardation factor and diffusion coefficient, the breakthrough times can be calculated knowing soil parameters and hydraulic head. For this, the theoretical curves have to be obtained earlier. In all these calculations, the soil porosity at Proctor's optimum dry density is taken. The hydraulic head is taken as zero (under diffusion only) or one meter (under advection and diffusion), because the survey of literature has shown that it can vary from 0 to 5m. The thickness of liner is normally would be about 1m.

1.6.1 Migration of ions in soils under given field conditions with diffusion only

Considering diffusion alone as responsible for migration of contaminating ions, the variation of relative concentration with distance after different periods of time can be calculated using the following equation

$$C/C_o = \text{erfc} (Rx/2Y(D_tR))$$

The variation of relative concentration with distance up to 1 m for ions in soil is calculated for different time periods taking the experimentally determined diffusion coefficient and retardation factor. For this a computer program is developed using MATLAB software.

1.6.2 Migration of ions in soil under given field condition considering both advection and diffusion

The effect of variation in diffusion coefficient and retardation factor of ions in migration of soil has been brought out. The migration of contaminants through compacted clay liners is essentially by diffusion in landfills where there is provision to collect or re circulate leachates from the bottom of the landfills. In landfills where there is no such provision leachate may build-up and the migration through the compacted clay liners is not only by diffusion but also under hydraulic advection. However, most landfills the leachate build-up may not be more than 1m. Hence migration of ions in

proposed liner has been studied under diffusion along with advection to assess any changes in trends of migration of ions compared to those under diffusion only.

1.7 Mathematical formulation to study the migration of ions under advection and diffusion

Considering both advection and diffusion as responsible for migration of contaminating ions the variations of relative concentrations of ions with time is calculated using the equation;

$$\frac{C}{C_o} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{Z - v_s t}{2\sqrt{(D_e t)}} \right) + \exp \left(\frac{R v_s Z}{D_e} \right) \operatorname{erfc} \left(\frac{Z + v_s t}{2\sqrt{(D_e t)}} \right) \right]$$

As in the previous case, here also, both the variation of (C/C_o) with time and variation of depth of arrival of time of (C/C_o) of 0.5 are calculated for different ions in proposed liner. For plotting the variation of relative concentration (C/C_o) with time, experimentally determined value of D (diffusion coefficient) and retardation factors are substituted for different both the chemical species considering 1 m as the thickness of liner. The computer program is modified to consider advective velocity of water and the program used with MATLAB software.

1.8 Rate of Migration of Ions in Soil Bentonite Liner

Liners are frequently constructed with natural materials serving as the primary barrier to liquid movement. Perhaps, it is impossible to provide complete containment of leachate generated from waste disposal facilities and the design of suitable clay liners require an estimation of potential rate of contaminant transport and the impact on the surrounding ground water system. However, prior to any quantification of contaminant transport it is required to establish controlling parameters by studying transport processes and mechanisms. The thickness of soil liner is designed knowing the rate of migration of contaminants through the soil (Syed Abu Sayeed Mohammed, Maya Naik., 2009).

2. MATERIALS AND METHODS

2.1 Materials used

Soil used

Clayey soil obtained from Mandur dumpsite in Bangalore was used in this study. The samples were collected by open excavation from a depth of 1 meter from natural ground. The soil so obtained has clay and silt content of 62%. The cation exchange capacity of soil is about 31meq/100g. The properties of soil used are listed in Table 1.

Table 1 Properties of Soil used

pH	9.3
Density, gm/cc	1.79
Moisture content, %	19
Optimum Moisture content, %	17
Gravels, %	1.32
Sand, %	41.23
Silt & clay, %	57.45
Specific gravity	2.45
Liquid Limit (%)	37
Plastic Limit (%)	19
Shrinkage Limit (%)	16.7
Permeability, cm/sec	2.4×10^{-6}

Bentonite Used

Bentonite procured from Indian Institute of Science, Bangalore was used in the present study. Bentonite is a natural clay mineral and is found in many places of the world. It belongs to 2:1 clay family, the basic structure in it is composed of two tetrahedrally coordinated sheets of silicon ions surrounding a sandwiched octahedral coordinated sheet of aluminium ions. It has excellent sorption properties and possesses sorption sites available within its interlayer as well as on the outer edges. The properties of bentonite used are summarize in Table. 2

Table 2 Physical Properties of Bentonite

Properties	Bentonite
Specific gravity	2.76
Liquid limit (%)	374
Plastic limit (%)	63
Plasticity index (PI)%	311
Sediment volume in water (ml/g)	16
Optimum moisture content (%)	45
Soil classification (ASTM D24487-unified Soil classification system)	CH-Fat clay
Percentage Clay fraction (%)	100

2.2 Experimental Setup

Influent Reservoir; It consists of a tank made of polyethylene with two openings. One at the top for transferring the synthetic source solution of iron and lead into it and the other at the bottom to collect effluent.

Column Assembly; The column assembly consists of Plexiglas cylinder of 11-cm long, 4-cm inner diameter and 1 cm thick wall. The Plexiglas cylinder is attached to the base plate, which houses a porous stone as shown in the Figure 1. The soil specimen of 4cm diameter and 10 cm height is compacted into the Plexiglas cylinder in three equal layers using a screw jack to ensure uniform compaction for the entire specimen. Once the soil sample was in place, one more set of porous stone are placed at the top and capped with top plate.

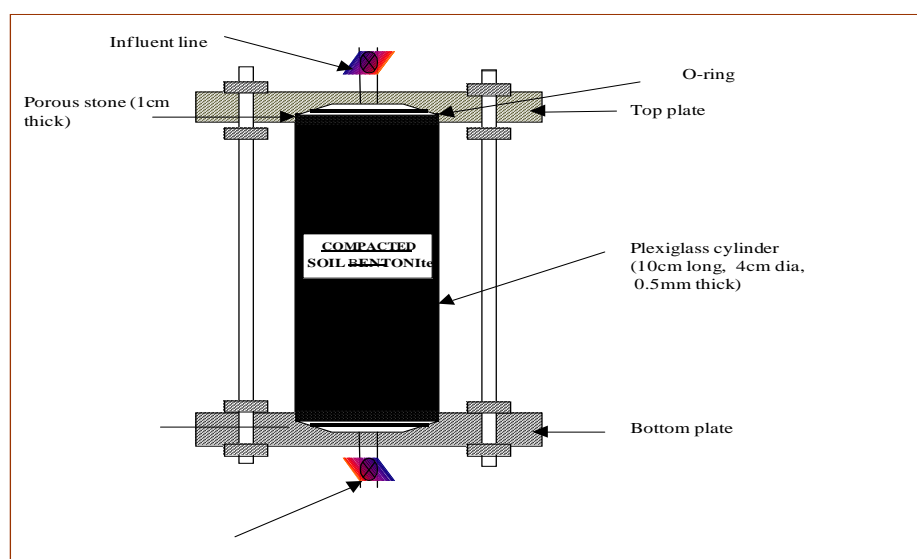


Figure 1 Experimental Set-Up of Column Soil Test

Effluent Collector; It consists of a jar covered at the top to avoid evaporation of collected leachate. The effluent collected in the collector is monitored regularly.

2.3 Preparation of soil sample and compaction

The oven dried soil is mixed with necessary amount of water separately as to prepare samples of required density. The soil is then compacted to required density by dividing the soil into 3 equal parts by weight and then, each part is compacted into Plexiglas cylinder.

2.4 Monitoring the effluent leachate

The desired solution is passed through the column. The volume of the effluent that comes out of the column with time was monitored at regular intervals and the concentrations of ions are measured. The interval selected varied with flow rate. The test is terminated once effluent concentration reaches influent concentration ($C=C_0$).

2.5 Chemical analysis of leachate

The chemical Analysis was performed by using AAS instrument. Dilutions were made to bring the concentration into instrument range.

3. RESULTS AND DISCUSSIONS

3.1 Diffusion coefficients of ions using experimental breakthrough curves of iron and lead ions

The aqueous diffusion coefficient describes how individual molecules and ions migrate, or randomly walkthrough subsurface soil and rocks, independent of water or carrier fluid. Diffusion coefficients often control the ultimate source of a contaminant that is how it comes out of the waste from or how it gets through some contaminant barriers. Once a contaminant gets out into the environment both diffusion and advection becomes the dominant transport processes.

By using the results of the column test the effective diffusion coefficient of ions are calculated by using different methods such as Ogata bank's method, time lag method and root time method.

The effective diffusion coefficients so determined are expected to take into consideration not only tortuosity of soils but also various attenuation processes that occur while the ions migrate through soils. To verify the extent to which they represent various processes that occur through the soils, knowing the seepage velocity in the column proposed to predict the breakthrough curves using the effective diffusion coefficients determined by different methods and soil properties and compare with actual breakthrough curves obtained. Theoretical curves are obtained considering both advection and diffusion as main processes for contaminant migration with time is determined by using the equation

$$\frac{C}{C_0} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{Z - vst}{2\sqrt{(D_e t)}} \right) + \exp \left(\frac{Rv_s Z}{D_e} \right) \operatorname{erfc} \left(\frac{Z + vst}{2\sqrt{(D_e t)}} \right) \right]$$

For plotting the variations of relative concentrations (C/C_0) with time, experimentally determined values of D (diffusion coefficients), velocity (v) are substituted for respective ions considering thickness of soil column used in the experiment and a computer program is developed using MATLAB

From this program, the variation of C/C_0 with time can be plotted for different chemicals length of the column as thickness through proposed liner. The curve thus determined are the theoretical curve and experimental values.

The breakthrough times are calculated for iron and lead ions for the proposed liner from theoretical and experimental curves and are presented in Table 3.

Table 3 Diffusion Coefficients of Ions

Ions	Literature	Ogata-Banks	Time-lag	Root-Time
IRON	2.22xE-6 cm ² /s	1.24xE-6 cm ² /s	3.08x8E-6 cm ² /s	2.706xE-6 cm ² /s
LEAD	3.92xE-6 cm ² /s	3.47xE-6cm ² /s	4.80xE-6 cm ² /s	3.500xE-6 cm ² /s

3.2. Migration of ions in soil bentonite liner considering diffusion alone

3.2.1 Migration of iron ion in soil bentonite liner

Figure 2 compares the theoretically obtained breakthrough curves of variation of relative concentration of iron ion with time using diffusion coefficients obtained by different methods for iron in soil bentonite with experimental curve. From the figure it is clear that the effect of variation in diffusion coefficient of iron obtained by different methods on breakthrough curves is marginal and none of the curves are close to the experimental curve. Thus the breakthrough time for iron with diffusion coefficient from theoretical curves for $C/C_0 = 0.5$ is in between 500 to 1000 hrs; the breakthrough time obtained experimentally from is 1666 hrs. It is clear that the theoretical breakthrough time is occurring earlier than the experimental breakthrough times.

There are considerable differences in the nature of curves while the theoretical curve indicates piston flow; the experimental curve indicates presence of attenuation/ retardation process. This shows that the effective diffusion coefficient alone, as calculated by different methods, is not adequate to describe breakthrough curves. This also indicates that the effective diffusion coefficient as calculated by different methods is not fully accounting all the retardation processes that may occur while the iron ion is migrating through soil.

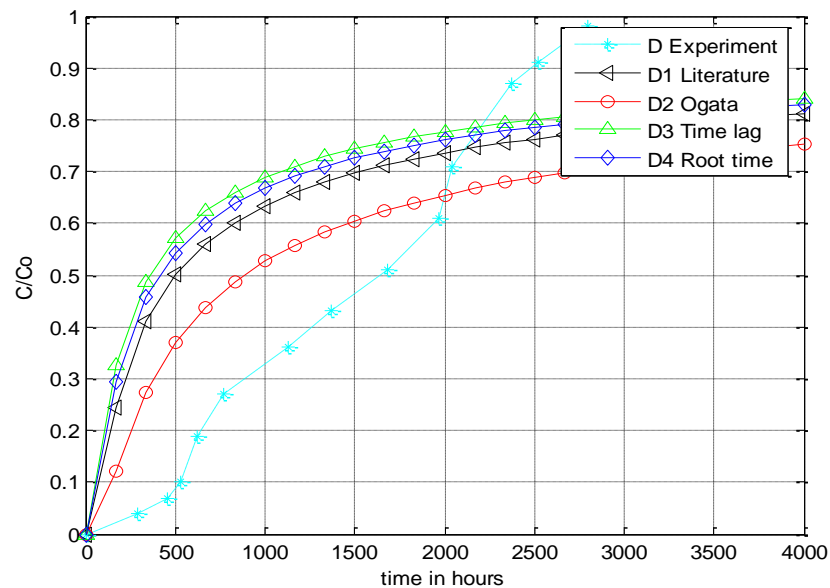


Figure 2 Comparison of theoretical breakthrough curves obtained using different diffusion coefficients with experimental curve for iron ion

3.2.2 Migration of lead ion in soil bentonite liner

Figure 3 compares the theoretically obtained breakthrough curves of variation of relative concentration of lead ion with time using diffusion coefficients obtained by different methods for lead in soil bentonite with experimental curve. From the figure it is clear that the effect of variation in diffusion coefficient of lead obtained by different methods on breakthrough curves is marginal and none of the curves are close to the experimental curve. Thus the breakthrough time for lead with diffusion coefficient from theoretical curves for $C/C_0 = 0.5$ is 350 to 500 hrs; the breakthrough time obtained experimentally is 1250 hrs. It is clear that the theoretical breakthrough time is occurring earlier than the experimental breakthrough times.

There is considerable difference in the nature of curves while the theoretical curve indicates piston flow, the experimental curve indicates presence of attenuation/ retardation process. This shows that the effective diffusion coefficient alone, as calculated by different methods, is not adequate to describe breakthrough curves. This also indicates that the effective diffusion coefficient as calculated by different methods is not fully accounting all the retardation processes that may occur while the lead ion is migrating through soil.

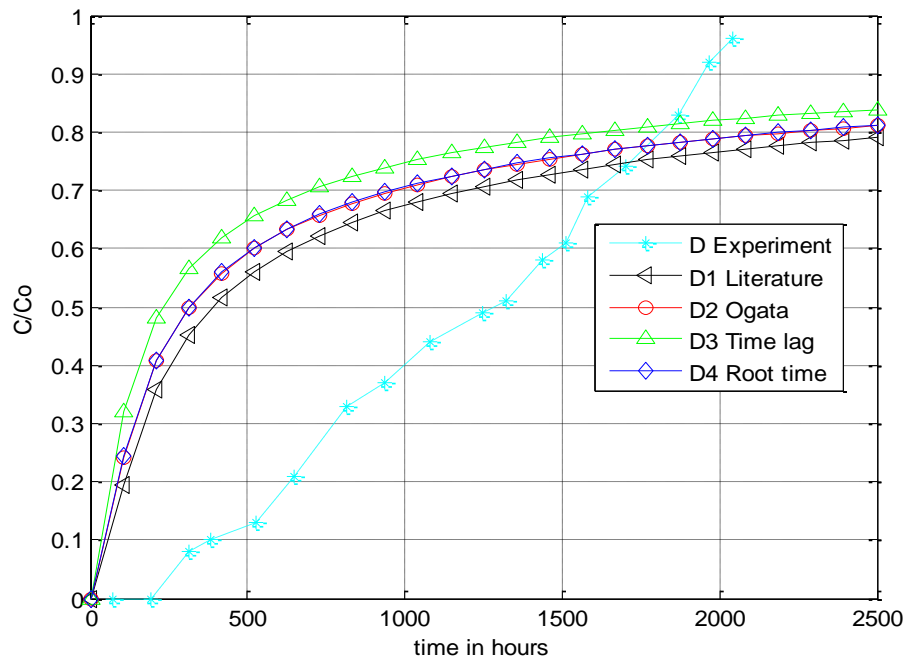


Figure 3 Comparison of theoretical breakthrough curves obtained using different diffusion coefficients with experimental curve for Lead ion.

3.3 Role of retardation factor in the prediction of experimental breakthrough curves of ions in soil

The breakthrough curves are drawn using advection diffusion equations considering experimentally determined effective diffusion coefficients. It has been observed that effective diffusion coefficient alone is not sufficient to predict breakthrough curves. To enhance the predictive capability, retardation factor, R_f that accounts all the retardation processes that occur while the ions are passing through soil is considered in the Ogata-Bank's equation.

Theoretically the breakthrough curves are important to reasonably assess the retardation factor, R_f from the detailed account of transport processes. The theoretical breakthrough curves for different ions are obtained using Ogata-Bank's equation

$$\frac{C}{C_o} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{R_f x - vst}{2\sqrt{(D_e t R_f)}} \right) + \exp \left(\frac{R_f v s x}{D_e} \right) \operatorname{erfc} \left(\frac{R_f x + vst}{2\sqrt{(D_e t R_f)}} \right) \right]$$

Calculated values of diffusion coefficients are determined by various methods, knowing velocity (v), and thickness of soil column used in the experiment and for different values of retardation factors have been developed with the MATLAB. The values of retardation factor, which gives theoretical curves close to the experimental breakthrough curve, are obtained.

3.4. Retardation factor of iron ion in soil bentonite mixture

Figure 4 shows the theoretically obtained breakthrough curves, using diffusion coefficients obtained by different methods, with retardation factor selected on trial and error for iron ion along with experimental curve. From the figure it is clear that all the theoretical curves agree reasonably well with the experimental curve. However some variation in the diffusion coefficients, even though the same retardation factor is used. Thus the breakthrough time for iron ion with any diffusion coefficient from theoretical curves for $C/C_0 = 0.5$ varies in the range of 800 to 1700 hrs; and the actual breakthrough time obtained by experimental curve is 1650 hrs. Relatively the curves obtained using diffusion coefficient obtained by Root time method is closer to the experimental breakthrough curve.

Compared to the theoretical curves obtained without retardation factor, the theoretical curves with retardation factor shows considerable variation between $C/C_0 = 0.5$ and 1.0., this is due to difference in the nature of breakthrough curves. The curves exhibit lesser characteristics of piston flow. The theoretical curves obtained without retardation factor showed earlier breakthrough time, whereas the curve in this case showed not only higher breakthrough times but also nearer to the experimental value.

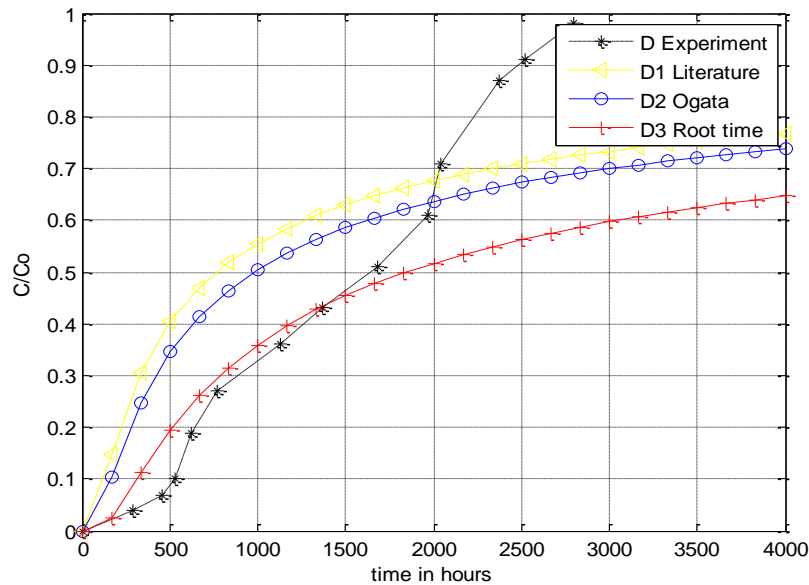


Figure 4 Comparison of theoretical breakthrough curves obtained using retardation factor and different diffusion coefficients with experimental curve for iron ion

3.5 Retardation factor of lead ion in soil bentonite mixture

Figure 5 shows the theoretically obtained breakthrough curves, using diffusion coefficients obtained by different methods, with retardation factor selected on trial and error for lead ion along with experimental curve. From the figure it is clear that all the theoretical curves agree reasonably well with the experimental curve except ogata bank's method. However some variation in the diffusion coefficients, even though the same retardation factor is used. Thus the breakthrough time for lead ion with any diffusion coefficient from theoretical curves for $C/C_0 = 0.5$ varies in the range of 500 to 1500 hrs; and the actual breakthrough time obtained by experimental curve is 1300 hrs. Relatively the curves obtained using diffusion coefficient obtained by Root time method is closer to the experimental breakthrough curve.

Compared to the theoretical curves obtained without retardation factor, the theoretical curves with retardation factor shows considerable variation between $C/C_0 = 0.5$ and 1.0, this is due to difference in the nature of breakthrough curves. The curves exhibit lesser characteristics of piston flow. The theoretical curves obtained without retardation factor showed earlier breakthrough time, whereas the curve in this case showed not only higher breakthrough times but also nearer to the experimental value.

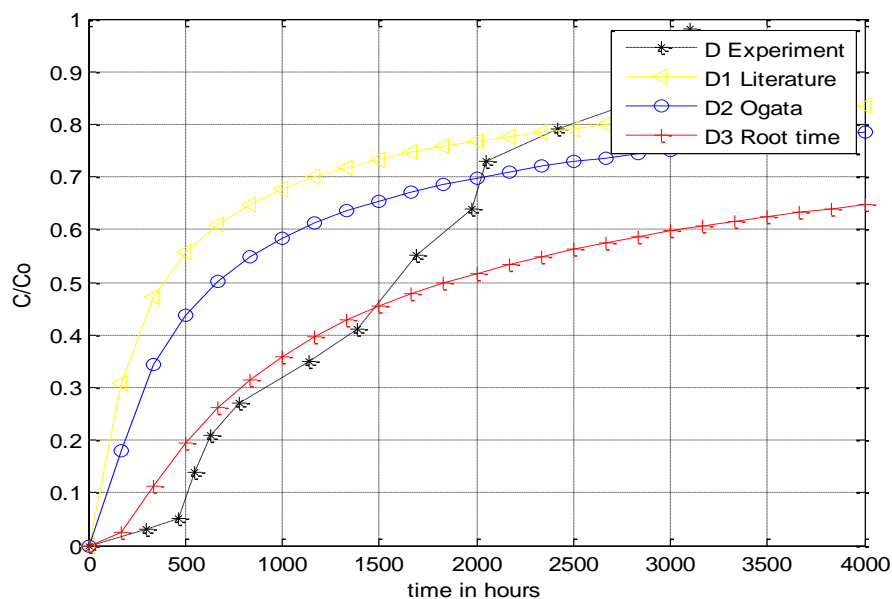


Figure 5 Comparison of theoretical breakthrough curves obtained using retardation factor and different diffusion coefficients with experimental curve for lead ion

From the above discussions the diffusion and retardation factors for lead and iron ions are listed as follows

Table 4 D_e and RF of Iron and Lead

Type of Contaminant	Diffusion Coefficient	Retardation Factor
Iron	$2.706 \times 10^{-6} \text{ cm}^2/\text{sec}$	5.5
Lead	$3.5 \times 10^{-6} \text{ cm}^2/\text{sec}$	4.5

3.6 Migration of Iron and Lead Ions Considering Diffusion Condition

Migration of Iron and Lead Ions Considering Diffusion Condition for 2m thickness liner

Figure 6 shows the variation of relative concentration with time for Iron and lead ion using respective diffusion coefficient in soil bentonite mixture for Iron and lead contaminating fluid and considering 2m as thickness of the liner. The breakthrough time for any relative concentration can be obtained in any soil. The curve showing the variation of breakthrough time of Iron and lead ion in soil bentonite mixture with respect to relative concentration, $C/C_0=0.5$, for lead break through occurs at 670 hours where as for iron it is 800 hours which clearly shows that iron ion is more retarded than Lead ion because of lower diffusion coefficient and higher retardation factor in the particular soil.

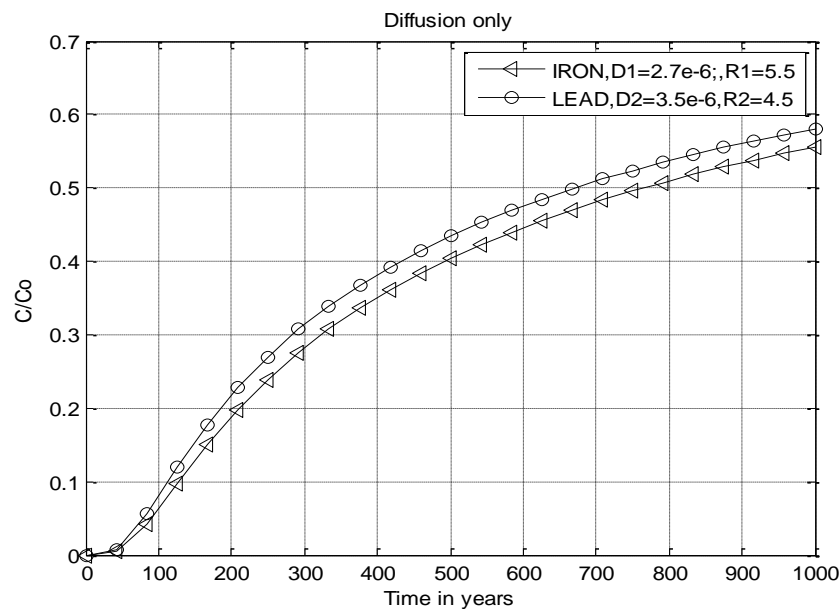


Figure 6 Variation of relative concentration with time for Iron and Lead considering diffusion only at 0.5m thickness

Migration of Iron and Lead Ions Considering Diffusion Condition for 1m thickness liner

Figure 7 shows the variation of relative concentration with time for Iron and lead ion using respective diffusion coefficient in soil bentonite mixture for Iron and lead contaminating fluid and considering 1m as thickness of the liner. The breakthrough time for any relative concentration can be obtained in any soil. The curve showing the variation of breakthrough time of Iron and lead ion in soil bentonite mixture with respect to relative concentration, $C/C_0=0.5$, for lead break through occurs at 390 hours where as for iron it is 500 hours which clearly shows that iron ion is more retarded than Lead ion because of lower diffusion coefficient and higher retardation factor in the particular soil.

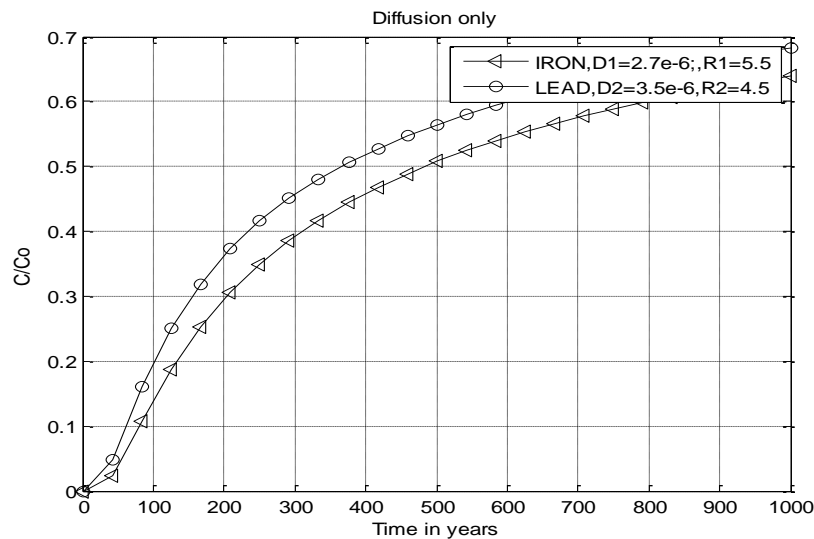


Figure 7 Variation of relative concentration with time for Iron and Lead considering diffusion only at 1m thickness

Migration of Iron and Lead Ions Considering Diffusion Condition for 0.5m thickness liner

Figure 8 shows the variation of relative concentration with time for Iron and lead ion using respective diffusion coefficient in soil bentonite mixture for Iron and lead contaminating fluid and considering 0.5m as thickness of the liner. The breakthrough time for any relative concentration can be obtained in any soil. The curve showing the variation of breakthrough time of Iron and lead ion in soil bentonite mixture with respect to relative concentration $C/C_0=0.5$, for lead break through occurs at 200 hours where as for iron it is 320 hours which clearly shows that iron ion is more retarded than Lead ion because of lower diffusion coefficient and higher retardation factor in the particular soil.

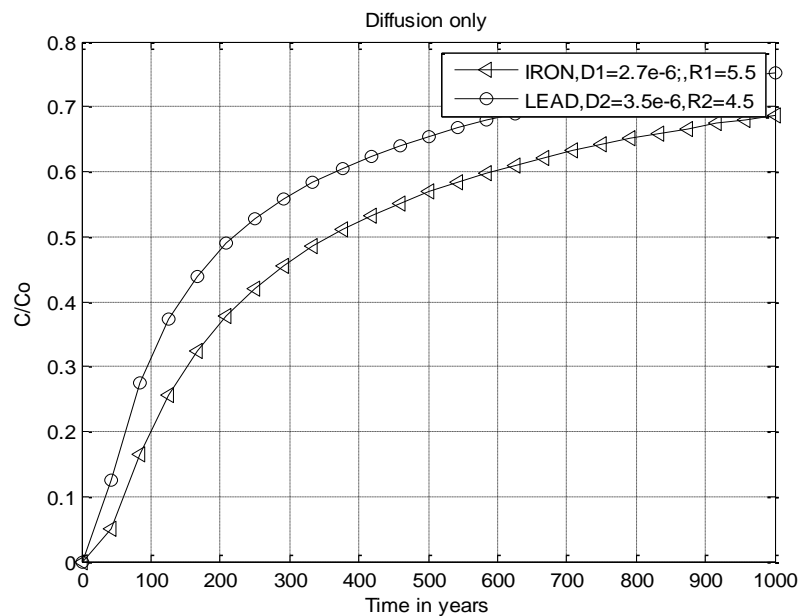


Figure 8 Variation of relative concentration with time for Iron and Lead considering diffusion only at 0.5m thickness

3.8 Migration of Iron and Lead Ions Considering both Advection-Diffusion Conditions

Migration of Iron and Lead Ions considering both Advection-Diffusion Conditions for 2m thickness liner

Figure 9 shows the variation of relative concentration of Iron and Lead with advection and with diffusion coefficients, diffusion coefficient reported in literature and the effective diffusion coefficient obtained from experiment. In proposed liner considering 2 m thickness of liner it is observing that the break through times increases steeply from 1 to 2 m thickness of liner because of nature of breakthrough times which increase steeply for a particular thickness. It can be observed that generally with any diffusion coefficient, the relative concentration increases with time. There can be infinite number of transit times depending on particular choice of relative concentration. The usual practice is to define transit time or breakthrough time as the time corresponding to relative concentration, C/C_0 of 0.5. As the thickness of liner increases, break through time also increases. The consequence of this behaviour is that the breakthrough time for C/C_0 of 0.5 are very nearly the same for both values of diffusion coefficient. Thus the effect of advection masks the effect of variation in diffusion coefficient. For the proposed liner of 2 m thickness, $C/C_0 = 0.5$ for lead break through occurs at 410 years and for iron occurs at 600 years. Thus the present study shows that the proposed liner can safely be used 500 years with 2 m thickness before the breakthrough of Iron and Lead ions occur.

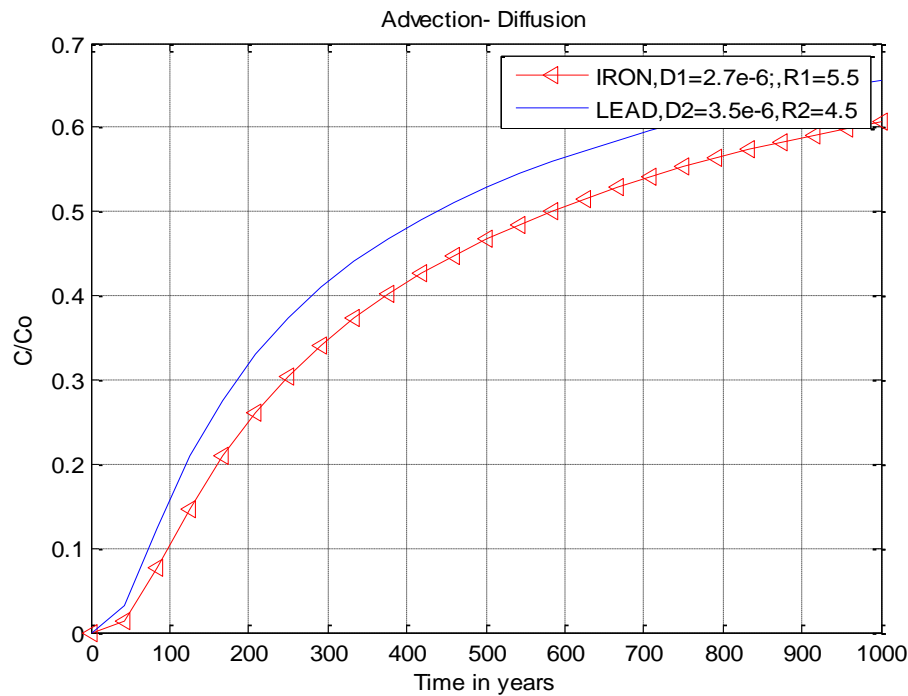


Figure 9 Variation of relative concentration with time for Iron and Lead considering both Advection-diffusion for 2m thickness

Migration of Iron and Lead Ions considering both Advection-Diffusion Conditions for 1m thickness liner

Fig.10 shows the variation of depth of arrival of C/C_0 of 0.5 front for Iron and Lead with 1 m thickness of liner considering both advection and Diffusion. It can be seen that the breakthrough concentration for Iron ion reaches bottom of Soil Bentonite liner of 1 m thickness within 210 years, and Lead ion takes about nearly 130 years. Comparing the breakthrough times obtained in case of diffusion alone the breakthrough times are reduced considerably in the present case.

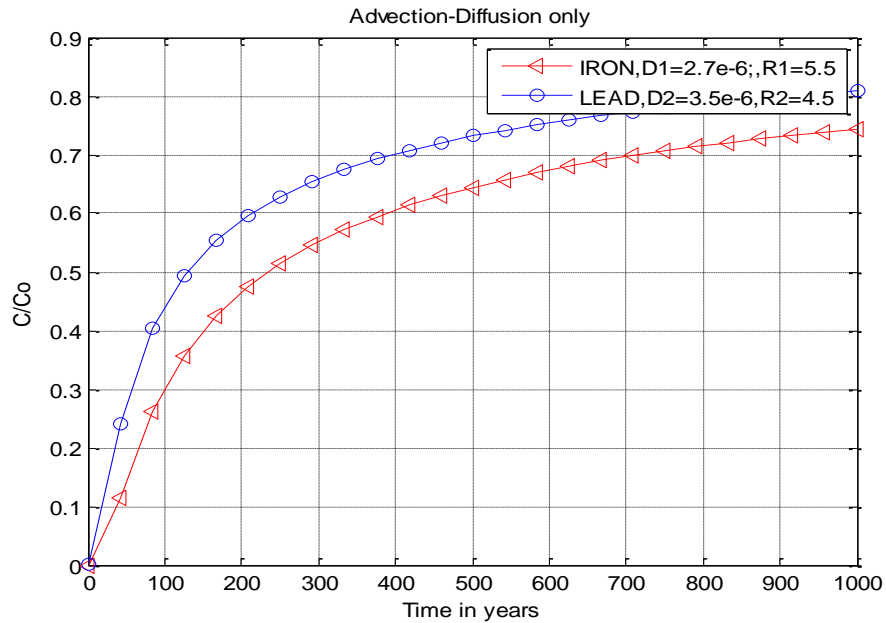


Figure 10 Variation of relative concentration with time for Iron and Lead considering both Advection-diffusion for 1m thickness

Migration of Iron and Lead Ions considering both Advection-Diffusion Conditions for 0.5m thickness liner

Fig.11 shows the variation of relative concentration of Lead with advection with diffusion coefficients in proposed liner considering 0.5m thickness of liner. As the thickness of liner decreases, break through time also decreases. It can be observed that, for the proposed liner of 0.5 m thick, breakthrough occurs at 50 years for lead ions and 75 years for iron ions.

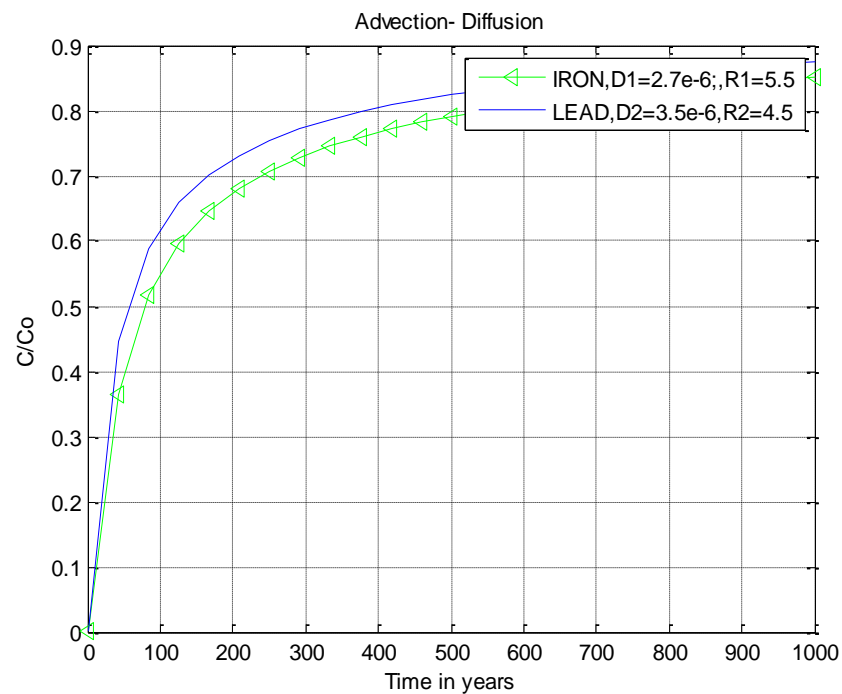


Figure 11 Variation of relative concentration with time for Iron and Lead considering both Advection-diffusion for 0.5m thickness

3.9 Comparison of breakthrough times of different chemical species considering diffusion alone and advection with diffusion

Table 5 Comparison of breakthrough times of different chemical species considering diffusion alone and advection and diffusion

Thickness of Liner (In meters)	Break through time at $C/C_0 = 0.5$ (In Years)	
	Diffusion Only	Advection with diffusion
For 2m thick Liner		
i) Iron	800	600
ii) Lead	670	410
For 1m thick Liner		
i) Iron	500	210
ii) Lead	390	130
For 0.5m thick Liner		
i) Iron	320	75
ii) Lead	200	50

4. CONCLUSIONS

From the current work the following major conclusions are as follows:

1. The breakthrough curves of iron and lead ions with time in soil are obtained using column tests.
2. The adsorption of ions is initially slow but increases rapidly with number of pore volumes or time.
3. To know the adequacy of diffusion coefficient alone, the theoretical breakthrough curves of ions in soil bentonite mixture are obtained using advection-diffusion equation using different diffusion coefficients for ion obtained by different methods and are compared with experimental curve. It is clear that prediction of breakthrough curve considering diffusion alone is not sufficient, hence there is a need to consider retardation factor too.
4. The transport of ions in soil bentonite mixture can be modelled by using both diffusion coefficient and retardation factor.
5. To obtain the values for retardation factor required, the breakthrough curve of ion in soil bentonite mixture using the ion and different diffusion coefficients as determined, are generated and compared with experimental breakthrough curves.
6. It has been observed that Iron and lead ions are better retarded in considered soil bentonite mixture under the processes of advection-diffusion. Thus the effect of variation in diffusion coefficients is governed by advection.
7. The theoretical breakthrough curves can be obtained using experimentally verified transport parameters, from which breakthrough times for any given thickness of the liner can be determined. This data helps to design liner thickness for a specified time.

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